Quenching of the Emission of Excited State [Ru(bipyridyl)₃]²⁺ by Heteropentalenes and Related Molecules

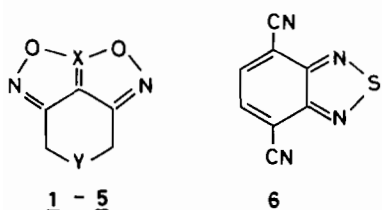JOHN S. CLAYTON, DUNCAN W. BRUCE, DAVID J. COLE-HAMILTON[§,+]

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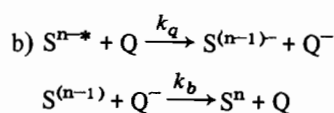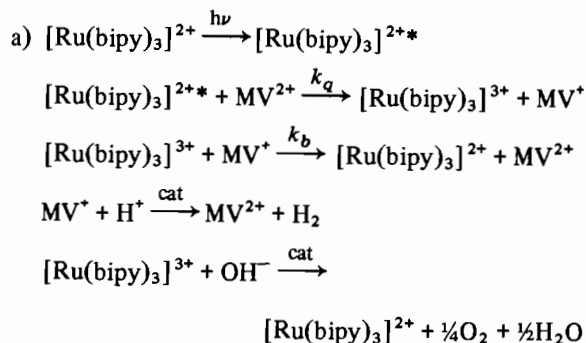The heterocyclic molecules **1–6** quench the emission of $[Ru(bipy)_3]^{2+*}$ (bipy = 2,2′bipyridyl) with

1 – 5   **6**

rate constants, k_q, of 3.2–4.1 × 10⁹ dm³ mol⁻¹ sec⁻¹, *cf.* 5.3 × 10⁸ dm³ mol⁻¹ sec⁻¹ for 1,1′-dimethyl-4,4′-bipyridinium dichloride (MV^{2+}).

The most commonly investigated systems for the photochemical decomposition of water involve a positively charged chromophore, *e.g.* $[Ru(bipy)_3]^{2+}$ [1] or $[ZnTPyMe]^{4+}$ (TpyMe = N,N′N″N‴-tetramethyltetrapyridylporphyrin) [2] and a multipositive electron transfer catalyst such as paraquat (MV^{2+}).

The key reactions of these species are shown in Scheme 1a for $[Ru(bipy)_3]^{2+}$ and it is clear that for successful hydrogen production the rate of the back reaction, k_b, must be as low as possible and higher efficiencies will be obtained if k_q is high. In practice, k_b is kept low because electrostatic repulsion between $[Ru(bipy)_3]^{3+}$ and $[MV]^+$ leads to charge separation, but electrostatic repulsion between $[Ru(bipy)_3]^{2+*}$ and $[MV]^{2+}$ means that k_q is low (5.5 × 10⁸ dm³ mol⁻¹ sec⁻¹) [3].

A possible alternative strategy would involve the use of a neutral electron transfer agent, Q, and a multi-negative chromophore (S^{n-}). The corresponding

reactions are then as shown in Scheme 1b and charge separation between Q^- and $S^{(n-1)-}$ keeps k_b low positive electron transfer catalyst such as paraquat (MV^{2+}).

a) $[Ru(bipy)_3]^{2+} \xrightarrow{h\nu} [Ru(bipy)_3]^{2+*}$

$[Ru(bipy)_3]^{2+*} + MV^{2+} \xrightarrow{k_q} [Ru(bipy)_3]^{3+} + MV^+$

$[Ru(bipy)_3]^{3+} + MV^+ \xrightarrow{k_b} [Ru(bipy)_3]^{2+} + MV^{2+}$

$MV^+ + H^+ \xrightarrow{cat} MV^{2+} + H_2$

$[Ru(bipy)_3]^{3+} + OH^- \xrightarrow{cat}$

$[Ru(bipy)_3]^{2+} + \frac{1}{4}O_2 + \frac{1}{2}H_2O$

b) $S^{n-*} + Q \xrightarrow{k_q} S^{(n-1)-} + Q^-$

$S^{(n-1)} + Q^- \xrightarrow{k_b} S^n + Q$

Scheme 1. a) The use of $[Ru(bipy)_3]^{2+}$ in the photochemical decomposition of water; b) possible use of a neutral electron transfer agent in water photolysis.

whilst k_q should be large since there is no net electrostatic interaction between Q and S^{n-}. In addition, neutral electron transfer catalysts should allow electron transfer across suitable membranes or vesicles.

As part of a survey of possible neutral electron transfer catalysts, we have studied the quenching of $[Ru(bipy)_3]^{2+*}$ by heteropentalenes of formula **1–5** [4], and by the related heterocyclic molecule, **6**, [5] since these are known to have redox properties which are somewhat similar to those of paraquat [6].

Table I shows the values of quenching rate constants k_q, for the various different heterocycles (obtained from Stern-Volmer plots), and their redox

TABLE I.

	X	Y	E°/Vᵃ	$k_q/10^9$ (dm³ mol⁻¹ sec⁻¹)
1	S	SO₂	−0.227	3.6
2	Se	S	−0.268	3.2
3	Se	CH₂	−0.273	3.7
4	S	CH₂	−0.375	4.0
5	S	S	−0.416	3.7
6			−0.490	4.1
MV²⁺			−0.044	0.53

ᵃ*vs.* NHE.

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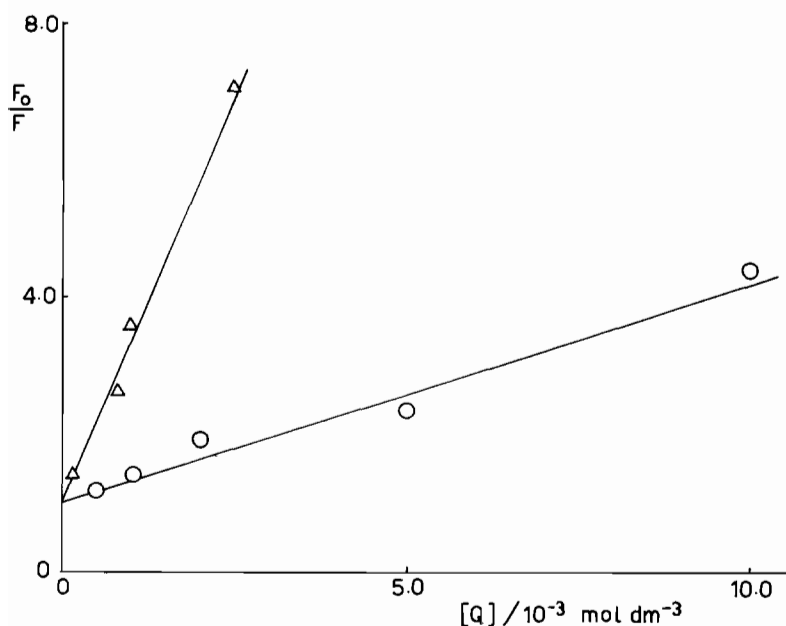+Sir Edward Frankland Fellow of the Royal Society of Chemistry 1984–5.

Fig. 1. Stern-Volmer plots of quenching of the emission of $[Ru(bipy)_3]^{2+*}$ by MV^{2+} (o) or by 5 ($\triangle$) $[Ru(bipy)_3^{2+}] = 5 \times 10^{-6}$ mol cm^{-3} in acetate buffer.

potentials; whilst Fig. 1 shows a comparison of a Stern-Volmer plot for quenching of $[Ru(bipy)_3]^{2+*}$ by 5 and by paraquat.

For all the neutral heterocyclic molecules, k_q is close to the diffusion controlled limit and up to an order of magnitude greater than that observed with paraquat and other positively charged quenchers.

Although correlations have been observed [7] between redox potential and quenching rate constants for different quenchers, we believe that these large increases of k_q compared with that of paraquat can be attributed to lack of electrostatic repulsion between the chromophore and the quencher. Evidence for this comes from the observations (i) that k_q for 6 is 8 times that for paraquat despite their having similar redox potentials and (ii) even for 1 which has the lowest redox potential k_q is 3 times that for, 1,1'-dibenzyl-4,4'-bipyridinium dichloride which has a redox potential of -0.33 V [7].

In view of this extremely efficient quenching behaviour and the known [6, 8] stability of the radical anions derived from these heterocyclic molecules, studies of their use as electron transfer catalysts are currently being carried out.

Acknowledgement

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